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This is a presentation for the American Chemical Society's Fall National Meeting, about the role of concurrent chemical and physical processes in determining the maximum use temperature of thermosetting polymers for aerospace applications.

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THE ROLE OF CONCURRENT CHEMICAL AND PHYSICAL PROCESSES IN DETERMINING THE MAXIMUM USE TEMPERATURE OF THERMOSETTING POLYMERS FOR AEROSPACE APPLICATIONS

29 August 2011

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Outline

- Background / Motivation
  - Unique Challenges in Analysis of High-Temperature Thermosetting Polymers
- Measuring T_g the Traditional Way
  - Effect of Heating Rate
  - Effect of Thermal Cycling
- Thermochemical vs. Thermomechanical Stability
- Alternative Ways to Find T_g
  - Extrapolation of diBenedetto equation
  - Extrapolation of Fox equation

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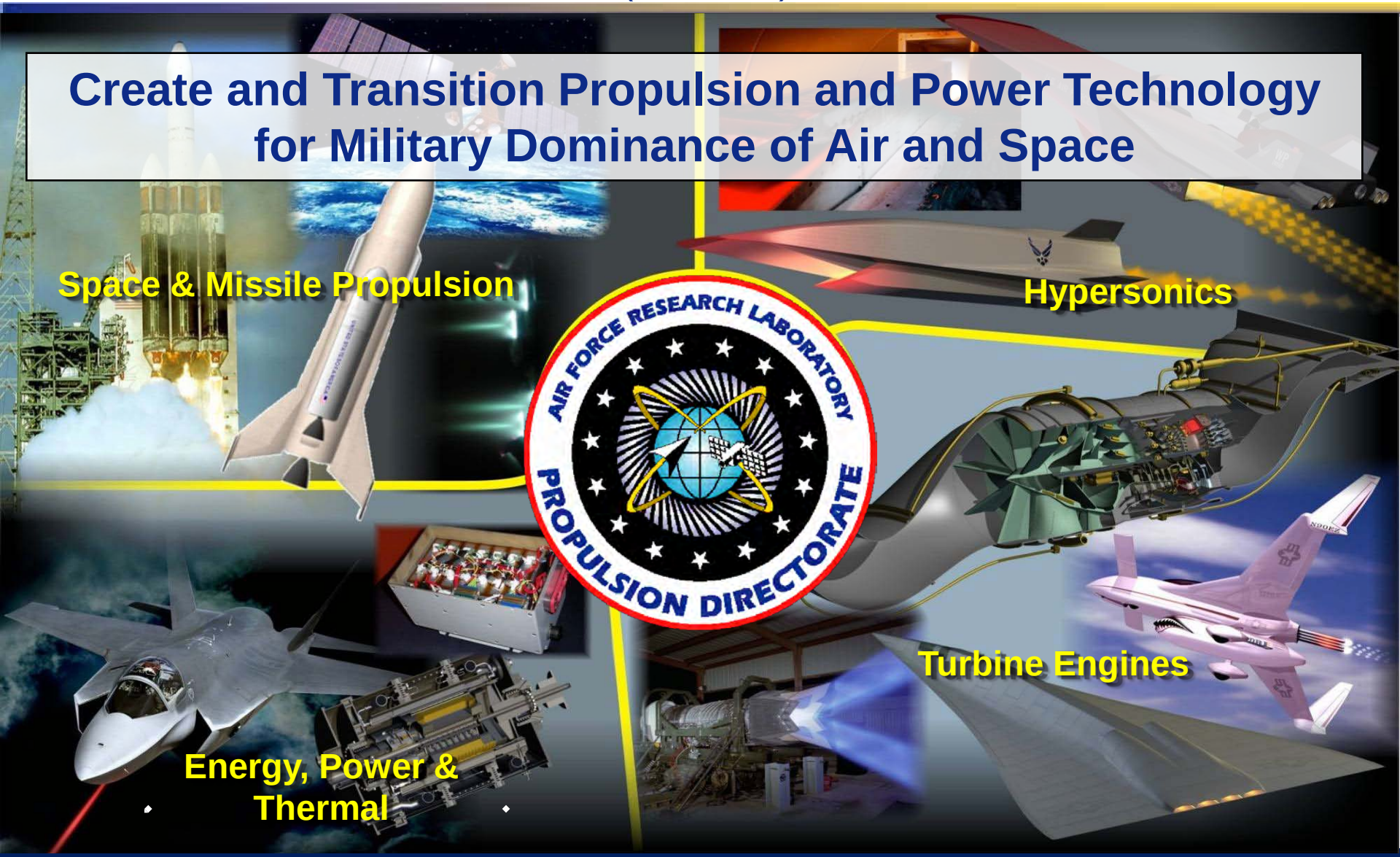
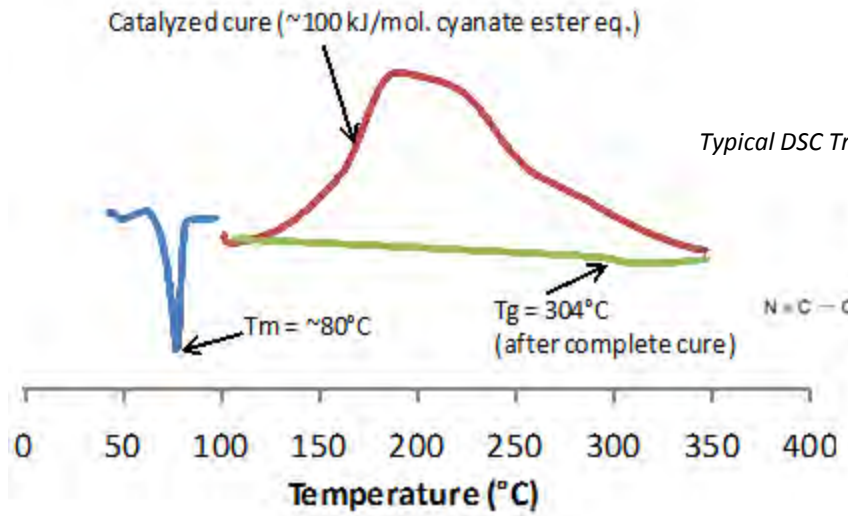
AFRL Propulsion Directorate

(AFRL/RZ)

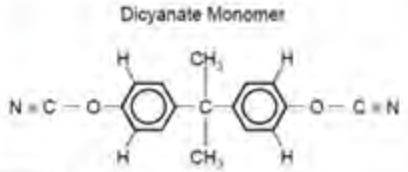
Create and Transition Propulsion and Power Technology for Military Dominance of Air and Space

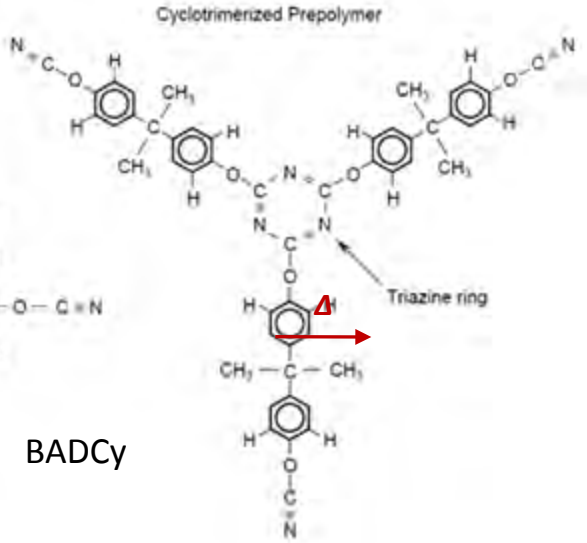


Cyanate Esters: Ideal for Studies of High-Temperature Thermosets



Typical DSC Trace of CEs





BADCy

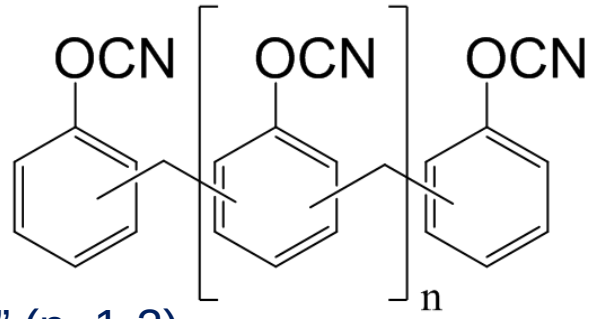
- **Single species reaction chemistry is "cleaner" than epoxy resin and well-understood; enables development of superior predictive models; readily catalyzed to cure at reasonable temperatures, providing a wide and tunable processing window**
- **Amenable to many different composite fabrication processes – filament winding, RTM, VARTM, compression molding, pultrusion; easy to make pure resin samples**
- **Minimal net shrinkage during cure; virtually no volatile released; good flame, smoke, and toxicity characteristics**
- **A wide variety of monomer architectures are available**
- **Highly relevant to propulsion systems, particularly those with short operational lifetimes; used in everything from microelectronics to space probes**

The Role of High-Temperature Polymers in Aerospace Propulsion

Photo credits: (clockwise from left: NASA, FAA, US Navy (Marvin E. Thompson), US Coast Guard. All images are public domain or freely distributed.

- **In general, for chemical propulsion, higher operating temperatures provide improved efficiency and better performance**
- **Organic materials in propulsion structures offer lower density, thus increasing delivered power per unit weight, but most often be insulated from the high-temperature portions of the propulsion system**
- **Higher maximum use temperatures for organic materials therefore reduce the need for insulation, allowing for more significant decreases in weight when using organic materials**
- **High-temperature polymer development therefore focuses on retaining mechanical properties over operationally relevant time scales at the highest possible temperature**

Cyanate Ester Monomers Used



"BADCy"

"PT-30" (n=1-2)

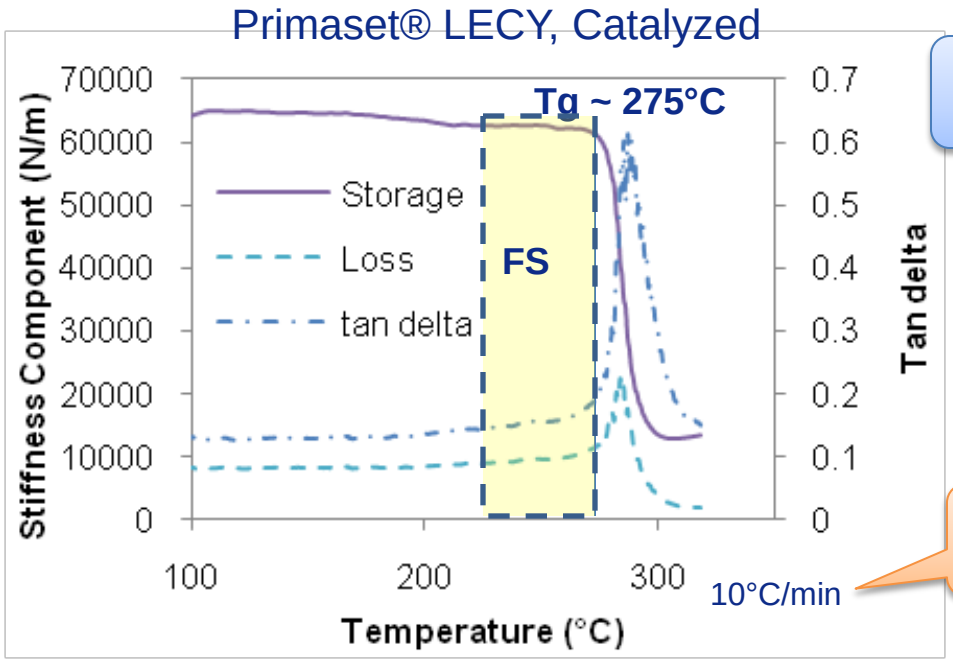
"LECy"

"FlexCy"

"SiMCy"

Catalyzed systems use:
160 ppm Cu(II) as Cu(II)AcAc with 2 phr nonylphenol,
All samples were melted, blended, and de-gassed for 30 min. prior to cure in silicone molds under N_2, cure schedules as indicated

Traditional Approach to Finding Maximum Use Temperature



Cured 150 °C for 1 hr + 210 °C for 24 hr

Why was this sample heated at 10 °C / min.?

- Use an oscillatory test of stiffness on a pure resin plaque or a composite
- Heat slowly to minimize temperature gradients and thermal lag in the sample
- Monitor the storage component of stiffness (as a proxy for total stiffness), define Tg as the temperature at which it “falls off a cliff”, subtract a factor of safety (up to 50 °C), and set the maximum use temperature equal to the result
- Test samples after exposure to various environmental factors (oxygen, water, etc.) to determine appropriate “knock down” for a given application

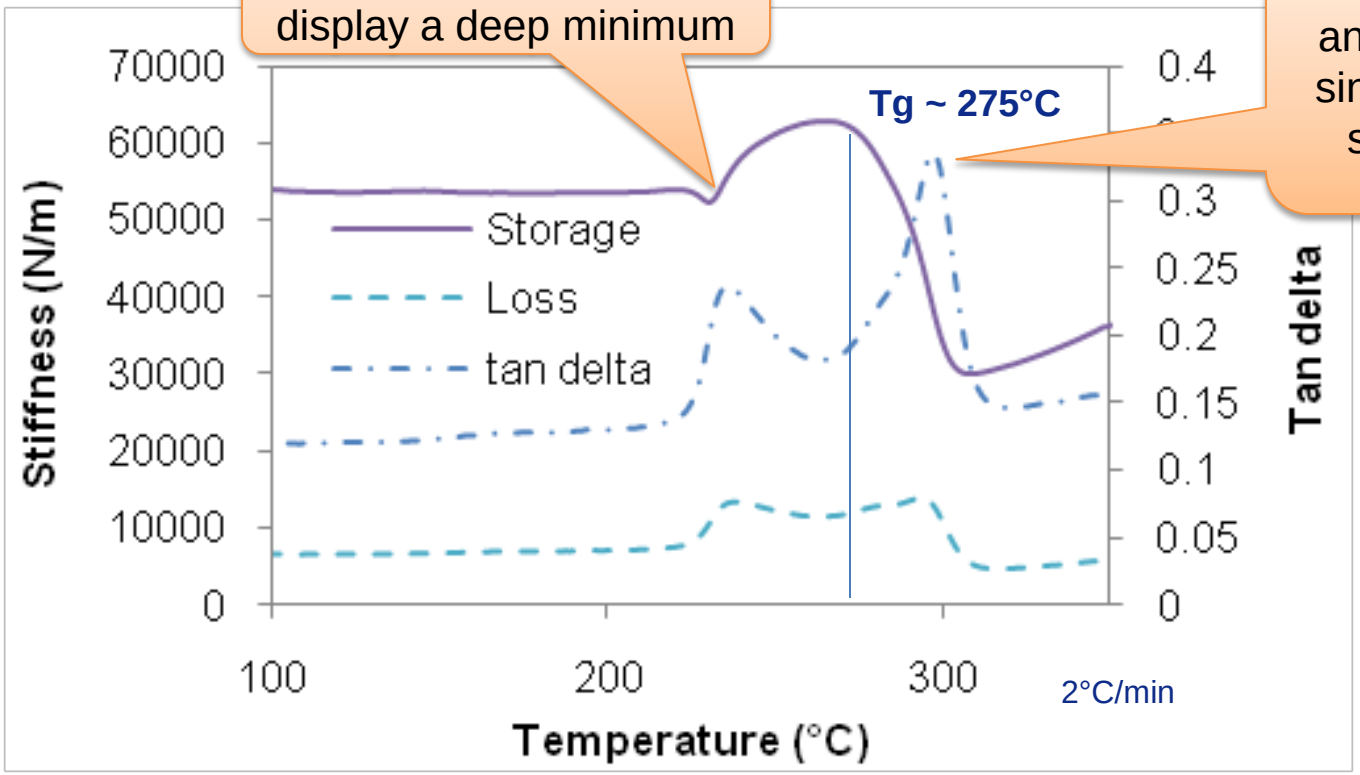
Effect of Heating Rate on Apparent Glass Transition Temperature

Primaset® LECY, Catalyzed

Cured 185 °C for 3 hr

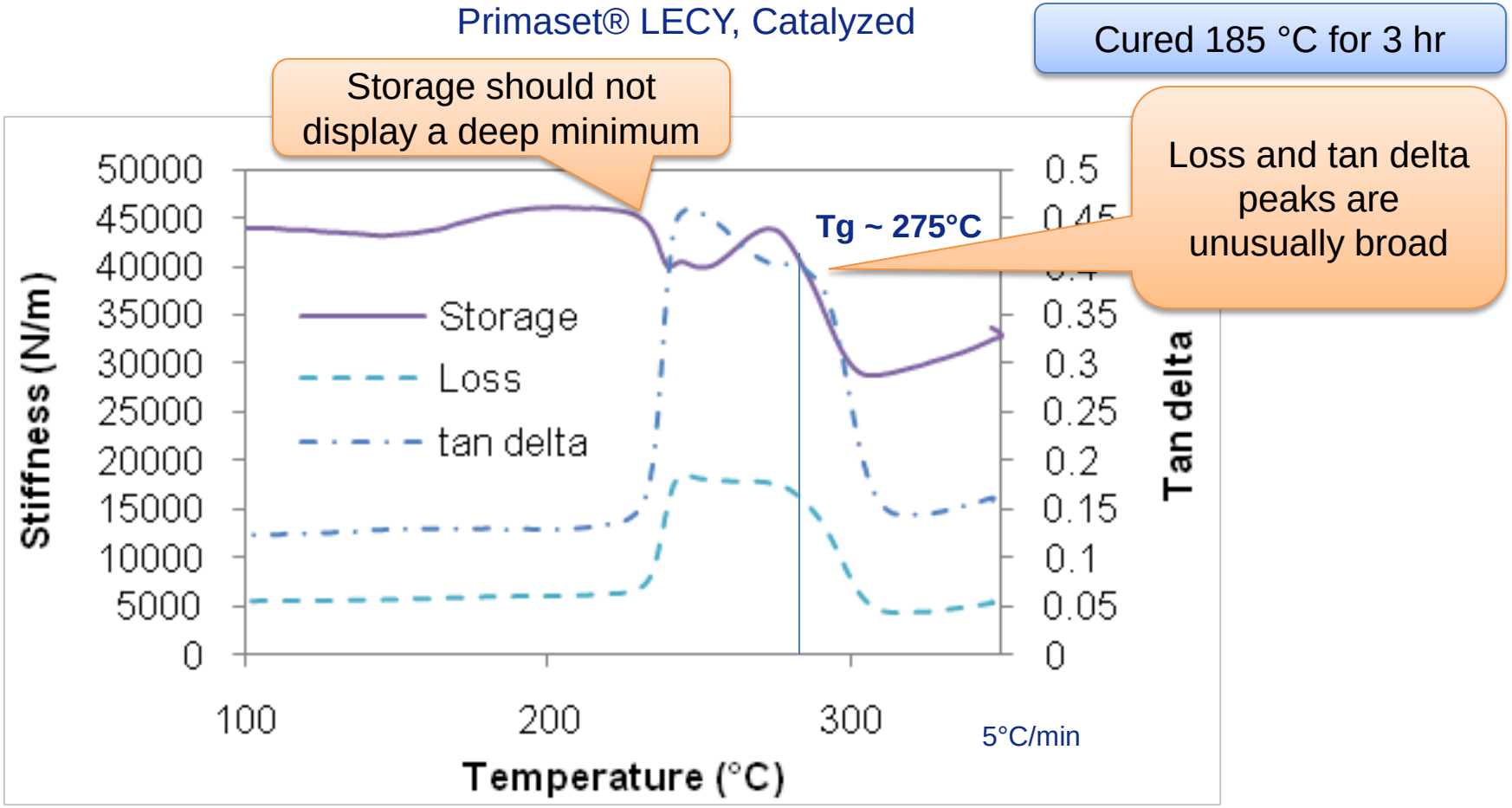
Storage should not display a deep minimum

Twin peaks in loss and tan delta in a single component system is very unusual



- Cyanate ester T_g values are usually sensitive to cure temperature, yet this data seems to suggest that cure conditions do not make much difference
- Low heating rates are supposed to make the data more reliable, but this data looks decidedly less reliable

Effect of Heating Rate on Apparent Glass Transition Temperature

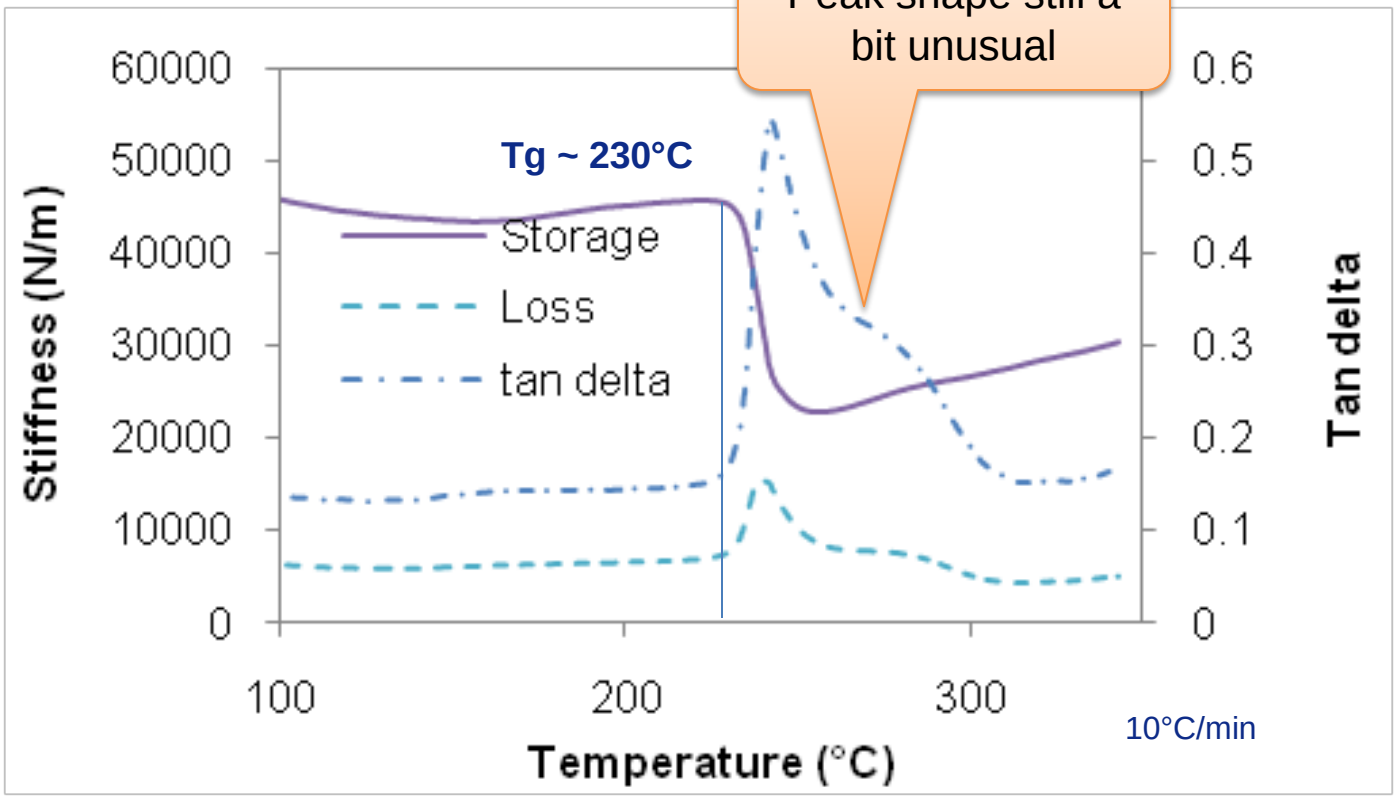


- Peak shapes are drastically different at the higher heating rate, and the primary transition is less pronounced

Effect of Heating Rate on Apparent Glass Transition Temperature

Primaset® LECY, Catalyzed

Cured 185 °C for 3 hr



- Not until the heating rate reaches 10 °C does the “as-cured” glass transition temperature become readily discernible; in this case the true effect of cure conditions on the glass transition temperature is observed

Why Does Heating Rate Make a Difference?

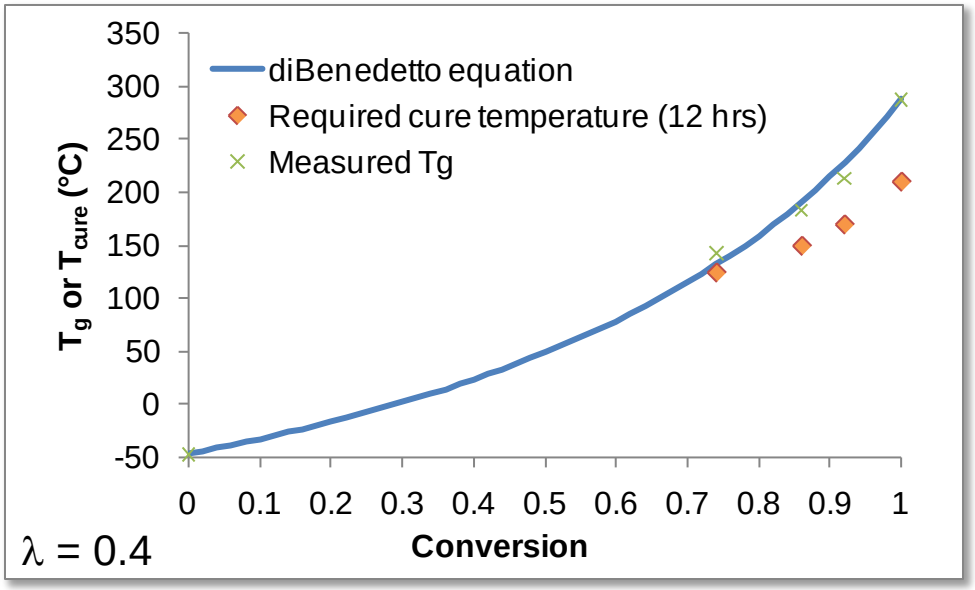
diBenedetto equation

$$\frac{T_{g-\chi} - T_{g-0}}{T_{g-100} - T_{g-0}} = \frac{\lambda\chi}{1-(1-\lambda)\chi}$$

χ= conversion, λ = empirical factor (can be derived from heat capacities)

Increase in T_g due to *in-situ* cure can be faster than the rate of heating

Primaset® LECY, Catalyzed

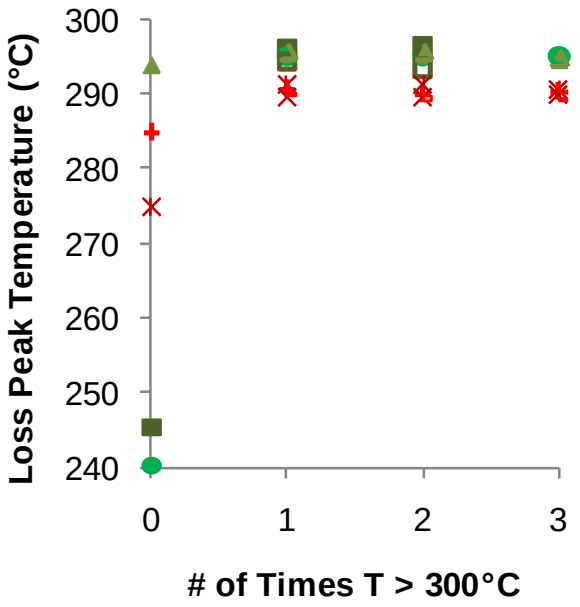


T_g and conversion measurements are by DSC

- Cyanate esters (and many other high-temperature thermosets) are “unusual” in that their glass transition temperatures can far exceed their maximum cure temperatures.
- This phenomena results from the steep dependence of glass transition temperature on conversion (via the diBenedetto equation) in systems that have the desirable qualities of high thermomechanical stability (high $T_{g\text{-}100}$) and ease of processing (low $T_{g\text{-}0}$)

Effect of Cycling on Measured T_g

Primaset® LECY, Catalyzed

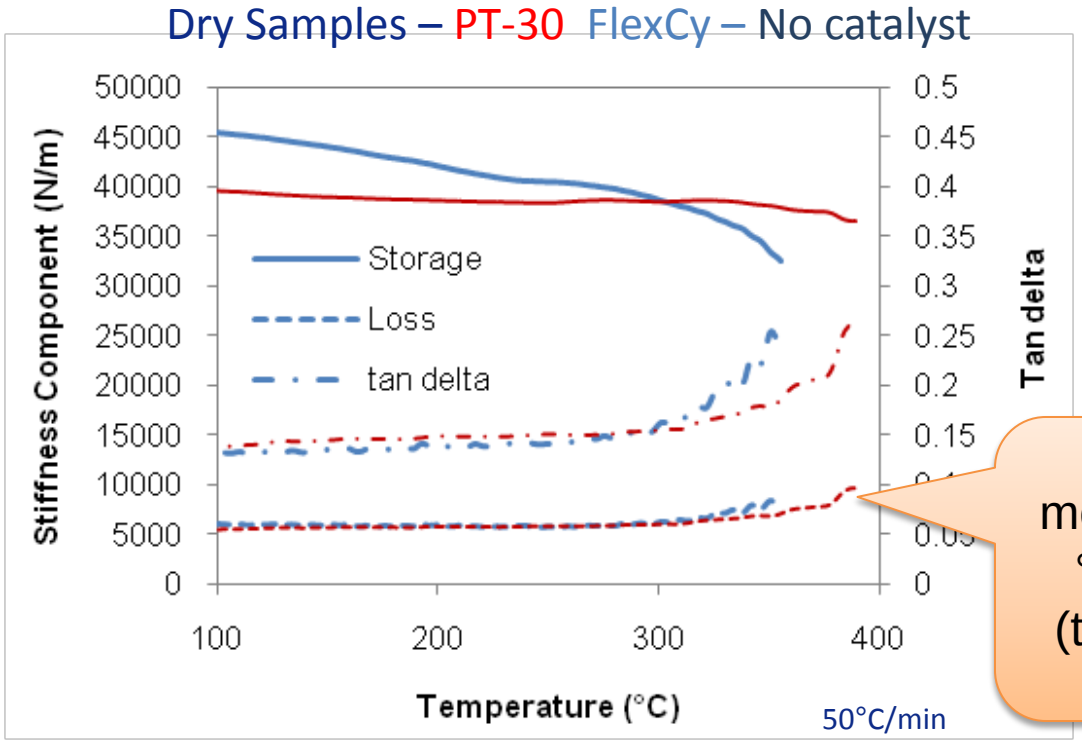


- Cured (185 °C) Heat 10 °C / min
- Cured (185 °C) Heat 5 °C / min
- Cured (185°C) Heat 2 °C / min
- Cured (185 °C) Cool 10 °C / min
- Cured (185 °C) Cool 5 °C / min
- Cured (185 °C) Cool 2 °C / min
- Post-Cured (240 °C) Heat 10 °C / min
- Post-Cured (240 °C) Heat 2 °C / min
- Post-Cured (240 °C) Cool 10 °C / min
- Post-Cured (240 °C) Cool 2 °C / min

All T_g values based on DTMA loss peak

- In contrast to “as-cured” glass transition temperatures, fully cured glass transition temperatures can be easy to measure, provided that the thermal cycling does not cause chemical degradation.
- The effect of final cure temperature on fully-cured glass transition temperature has been previously noted (Goertzen, W. K.; Kessler, M. R. *Composites: Part A* **2007** 38, 779)

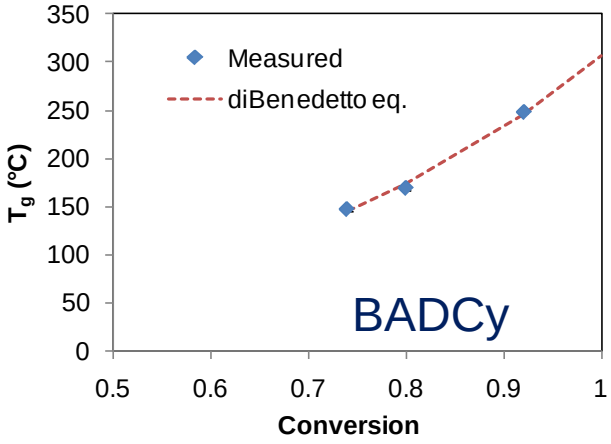
Effect of Chemical Degradation

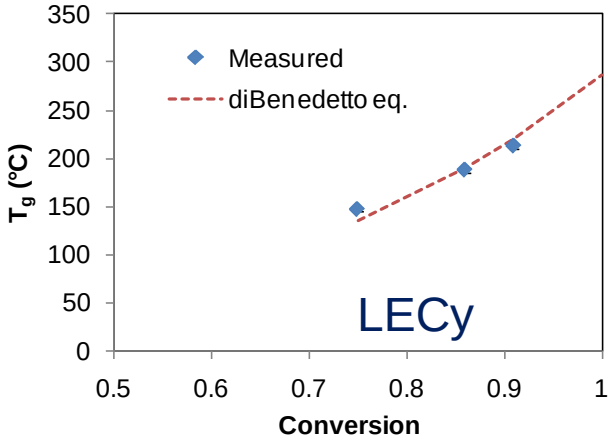


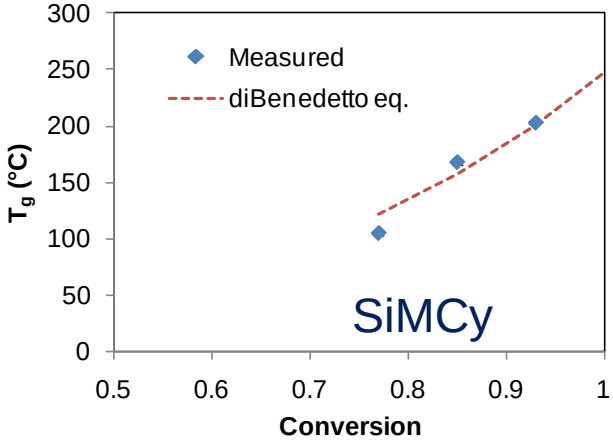
PT-30 T_g measured at 400 °C by Marella (thesis, Drexxel Univ., 2008)

- A complete glass transition was observed for neither system due to chemical degradation, which forced early termination of the experiment
- Though from a “use temperature” perspective, the dynamic mechanical technique is sufficient, from a basic science perspective it would be highly useful to separate the effects of mechanical softening from those due to chemical degradation

Estimate of T_g via diBenedetto Equation





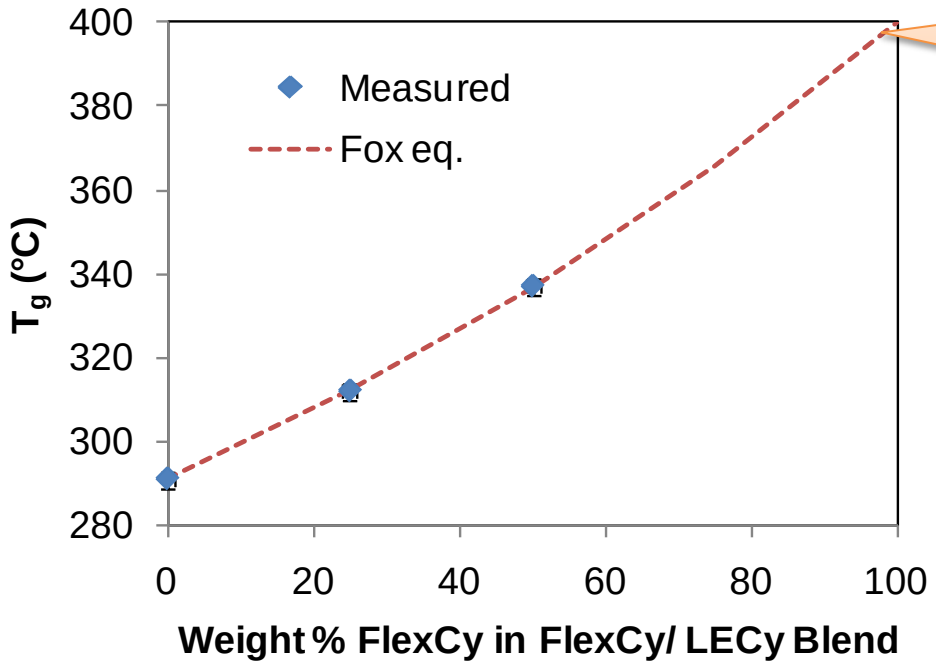


	Estimated Tg (°C)	Actual Tg (°C)
BADCy	307	304
LECy	286	290
SiMCy	247	260

All T_g values based on DTMA loss peak
All samples include catalyst

- For all three cyanate esters studied, extrapolation of the diBenedetto equation with $\lambda = 0.4$ (as determined experimentally from blend studies) showed agreement to within 15 °C. This technique is limited by the difficulty in separating DSC signals due to cure and degradation at very high temperatures.

Estimate of T_g via Fox Equation



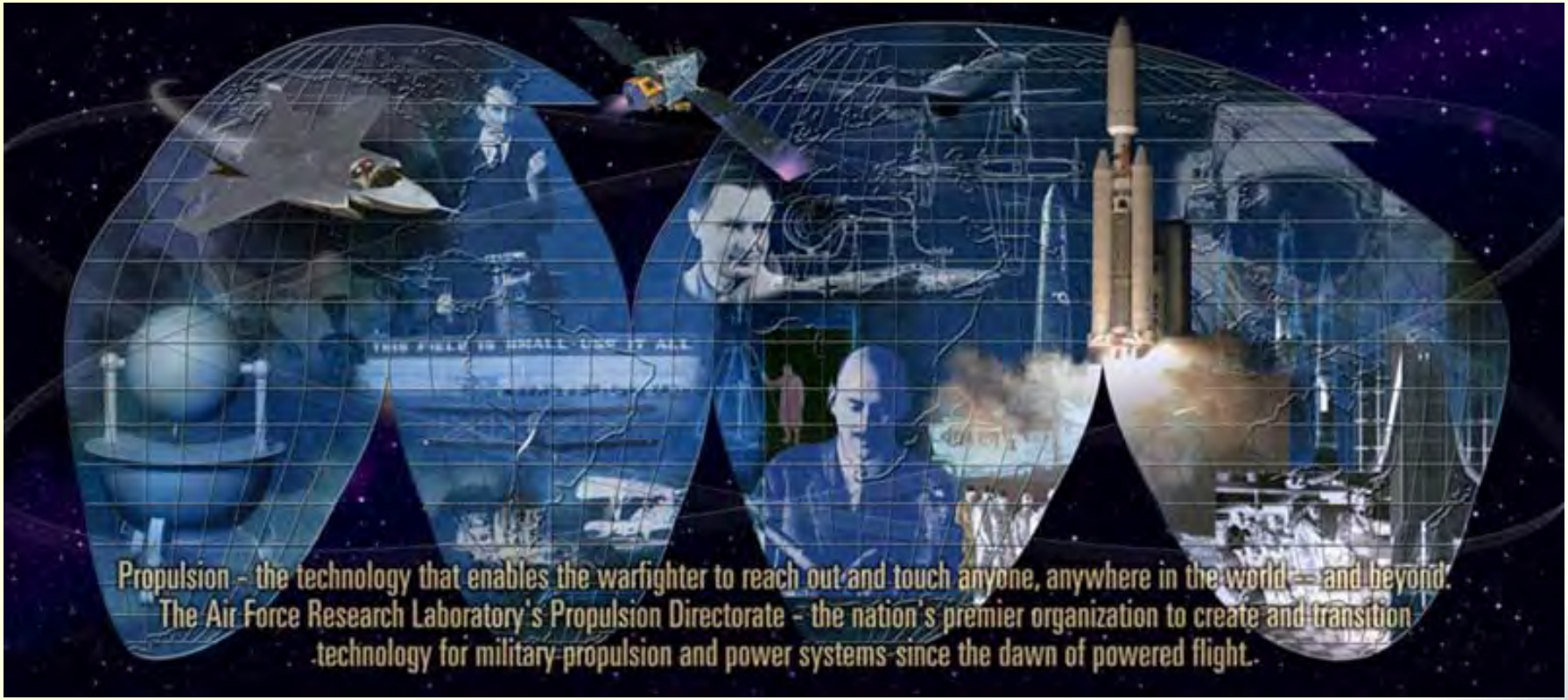
Estimated FlexCy
Tg = 400 ±10 °C

All T_g values based on DSC step transition mid-point; no catalyst included

- Fit to Fox equation appears to be good. Significant extrapolation is required.
- The use of modulated DSC may allow for measurement of higher Tg values (limited to about 350 °C in regular DSC).
- Recent cyanate ester blend studies have shown deviation of up to 15 °C from values predicted by Fox equation when pure component T_g values are known, thus this technique needs additional validation to establish its accuracy.

Summary

- Though essential for aerospace applications, the determination of maximum use temperatures for high-temperature thermosetting polymers presents challenges not encountered in more conventional composite matrix resins.
- Characterization of glass transition temperatures by traditional dynamic mechanical analysis methods at low heating rates can be severely affected by in-situ cure when maximum cure temperatures are below glass transition temperatures.
- Dynamic mechanical methods do not distinguish between thermochemical and thermo-mechanical instability, even though such distinctions may be important for studies of structure-property relationships.
- Alternative methods of estimating glass transition temperatures, based on extrapolation of the Fox equation or the diBenedetto equation, may be used to estimate glass transition temperatures that are higher than actual exposure temperatures, thereby avoiding difficulties associated with in-situ cure or thermochemical degradation.



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